The Photocycloaddition of Carbonyl Compounds to Allenes

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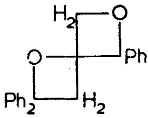
THE photocycloaddition of the carbonyl moiety to olefins has been studied extensively in recent years.[1] There are, however, few reported examples of such additions to other types of unsaturated systems.[2] We have found that carbonyl compounds in an excited state can add to allenes, giving the first examples of the 2-alkylideneoxetan and 1,5- and 1,6-dioxaspiro[3,3]heptane ring systems.

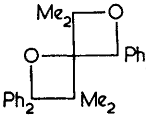
Irradiation of benzene solutions of benzophenone (0·05 M) and allene (*ca.* 1 M) with a high-pressure mercury arc led to the formation of (I) in 38% yield (based on benzophenone).[3] Similarly, (II—IV) were found upon irradiation of benzophenone (0·1 M) in the presence of tetramethylallene (0·12 M) in 43, 22, and 12% yield respectively.

When acetone (solvent) and tetramethylallene (0·1 M) are subjected to these conditions, the products (V—VII) (8, 51, and 27% yield based on tetramethylallene) result.



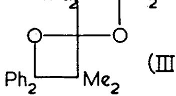
(I)

m.p. 129·5 – 130°



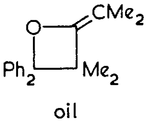
(II)

m.p. 150·5 – 152·5°



(III)

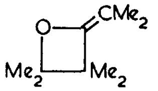
m.p. 152 – 154°

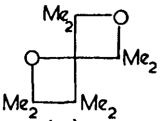


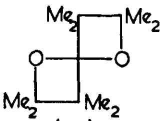
(IV)

oil

Products (I—IV) were isolated by column chromotography on alumina while (V—VII) were obtained by preparative vapour-phase chromotography. Satisfactory combustion analyses were obtained on all of these new compounds. Compounds (IV) and (V) were not stable at room temperature and had to be analyzed promptly or the results were spurious; the other compounds were stable. The structures were established primarily by n.m.r. spectra. The assignment of (III) rather than the other possible symmetrical structure (the 2,6-dioxa-system) was made by treating this adduct with ethanolic hydrogen chloride to give 1,1-dimethyl-2,2-diphenylethylene among the products. Both (VI) and (VII) have four different types of methyl groups; however, the distinction between them was obvious upon examination of the n.m.r. spectra of the corresponding products (VId and VIId) from perdeuteroacetone. Three peaks (two of equal intensity and half of the third) were observed for (VId), while (VIId) had only two peaks (of equal intensity).


(V)
oil


(VI)
m.p. 84·5–86·0°


(VII)
m.p. 36–38°

All of the cycloaddition products can arise from an initial attack by the oxygen of the carbonyl n,π^*-state on the central carbon of the allene linkage (no 2,6-dioxaspiro[3,3]heptanes were detected). This is in contrast to the reaction of ordinary free-radicals with allene where both terminal and central additions have been observed.[4] When the excited state of an $\alpha\beta$-unsaturated carbonyl compound reacts with an olefin[5a–c] or allene,[5c–e] the addition takes place at the carbon–carbon double bond giving a cyclobutane or methylenecyclobutane adduct.

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[1] (a) D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Letters*, 1964, 1425; (b) N. C. Yang, *Pure Appl Chem.*, 1964, **9**, 591.

[2] (a) G. Büchi, J. T. Kofron, E. Koller, and D. Rosenthal, *J. Amer. Chem. Soc.*, 1956, **78**, 876; (b) L. A. Singer and P. D. Bartlett, *Tetrahedron Letters*, 1964, 1887.

[3] The major product (47%) was benzpinacol which we believe to be formed by hydrogen abstraction from propyne present as an impurity in commercial allene.

[4] E. A. I. Heiba, *J. Org. Chem.*, 1966, **31**, 776; and references therein.

[5] (a) P. deMayo and H. Takeshita, *Canad. J. Chem.*, 1963, **41**, 440; (b) P. E. Eaton, *J. Amer. Chem. Soc.*, 1962, **84**, 2344, 2454; (c) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *ibid.*, 1964, **86**, 5570; (d) P. E. Eaton, *Tetrahedron Letters*, 1964, 3695; (e) W. Guthrie, A. Philipp, Z. Valenta, and K. Wiesner, *ibid.*, 1965, 2945.